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Project Summary

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ORIGINAL

Determination of Dithiocarbamate Pesticides in Wastewaters

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A method was modified and validated for the determination of dithiocarbamate pesticides in wastewaters. The developed method consists of sample pH adjustment to pH 12; removal of indigenous carbon disulfide (CS_2) by purging in a vortex evaporator; acidification of the sample to hydrolyze dithiocarbamate pesticides to form CS_2; extraction of the CS_2 from the sample into hexane; and determination of the CS_2 by gas chromatography using a Hall detector in the sulfur mode.

The hydrolysis and CS_2 extraction procedures used in this method were developed during research conducted under EPA Contract No. 68-03-2956. The purpose of these studies conducted under EPA Contract No. 68-03-1760 was to develop a simple, effective method to remove indigenous CS_2 from a water sample prior to dithiocarbamate determination, and to validate the total analysis method. Minimal dithiocarbamate stability studies were also conducted to aid in determining optimal pH ranges for sample storage and preparation.

The final method was validated using 13 dithiocarbamate pesticides. The method detection limit (MDL) and an analytical curve were determined for each dithiocarbamate in reagent water. The method was then applied to a wastewater obtained from a manufacturer of a dithiocarbamate in order to determine the precision and accuracy of the method.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The group of dithiocarbamates used for method development and validation purposes was comprised of 17 compounds: amobam, Busan 40, Busan 85, EXD, ferbam, KN-methyl, mancozeb, maneb, metham, nabam, nabonate, Niacide, polyram, sodium dimethyldithiocarbamate (NaDMDTC), thiram, zineb, and ziram. The method was found to be unsuitable for the determination of polymeric dithiocarbamates such as maneb, mancozeb, and polyram. The remaining 13 dithiocarbamates were used for method validation. the method is based on the determination of CS_2 which is evolved from the dithiocarbamate moiety upon acid hydrolysis. The method is not specific for dithiocarbamates.

In general, dithiocarbamates are moderately stable in water under very basic conditions. A CS_2 generation method followed by determination of the CS_2 by GC-Hall analysis was the selected approach. The CS_2 is generated from the dithiocarbamate upon treatment with a stannous chloride ($SnCl_2$)/hydrochloric acid (HCl) mixture. The $SnCl_2$ is present to reduce any thiuram disulfide to the dithiocarbamate and to inhibit oxidation of the dithiocarbamate prior to its decomposition. The generated CS_2 is extracted from the water into hexane during the decomposition process and determined by GC using a Hall detector in the sulfur mode. This procedure has proven to be more sensitive and easier than previously developed colorimetric detection methods. A cleanup method was

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developed to remove any CS_2 originally present in the wastewater. This cleanup method involves purging of the CS_2 from the sample using a vortex evaporator.

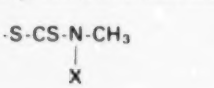
Cleanup

A cleanup method was necessary to remove indigenous CS_2 from the water sample prior to hydrolysis of dithiocarbamates. If this is not done, artifically high levels of dithiocarbamates would be determined in the samples. A hexane extraction step at basic pH was originally developed for the purpose under EPA Contract No. 68-03-2956. This method was found to be effective, but proved to be tedious and time-consuming when processing many water samples. Two alternative cleanup methods were identified based on the fact that CS_2 is easily purged from water: removal of CS_2 from water using a vortex evaporator and removal of CS_2 from water by purging with nitrogen.

Use of a vortex evaporator to remove the CS_2 from the aqueous media was slightly more efficient than purging with nitrogen, presumably because dispersion of the nitrogen gas from the 19-gauge needle through the sample was not sufficient for effective CS_2 removal.

Dithiocarbamate Stability Studies

Some of the dithiocarbamate pesticides were not stable in pH 9 buffer, especially compounds with the following structures:



$X = O^-, H$

One of the dithiocarbamate pesticides with this structure, Busan 40, was found to be particularly unstable in pH 9 buffer. This instability became more pronounced as the Busan 40 concentration in the buffer was lowered.

Method Detection Limit

MDLs were determined by the procedure recommended by EPA/EMSL which defines MDLs in terms of a test that the data show values greater than zero at the 99 percent confidence level. MDLs were calculated from data obtained from the analysis of seven replicate buffer samples spiked at the 10 μg/L level with the appropriate dithiocarbamate pesticide.

Analytical Curves

Reagent water was spiked in duplicate with the individual dithiocarbamate pesticides at the 10, 50, 100, 500, and 1000 μg/L levels. Recoveries of these dithiocarbamates were determined using the dithiocarbamate analysis method and analytical curves were generated by plotting the amount of dithiocarbamate spiked into the samples versus the calculated amount recovered from the samples. Recoveries for these nonpolymeric dithiocarbamates were generally greater than 85 percent with the exceptions of EXD, nabam, and nabonate.

Method Validation in Wastewater

A wastewater sample was obtained from a manufacturer of a dithiocarbamate pesticide and diluted 1000:1 with Columbus secondary POTW effluent prior to use in validation studies. Seven aliquots of this diluted wastewater were then analyzed to determine background dithiocarbamate levels. The diluted wastewater was then spiked at the 50 and 500 μg/L levels with the individual dithiocarbamate pesticides and analyzed. Seven replicate extractions were performed at each concentration level. Recoveries of dithiocarbamates, corrected for background dithiocarbamate levels, were then calculated.

The diluted dithiocarbamate wastewater contained low levels of dithiocarbamate, 4.5 to 6.2 μg/L, depending upon the molecular weight of the dithiocarbamate analyzed. Method validation data for the dithiocarbamate pesticides in wastewater are given in Table 1. Recoveries for these nonpolymeric dithiocarbamates were generally greater than 82 percent with the exceptions of EXD, nabam, and nabonate.

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Table 1. *Results of Method Validation Study for Dithiocarbamate Pesticides in Wastewater*

Compound	Background Level, µg/L	Amount Spiked, µg/L	Average Amount Recovered, µg/L	Standard Deviation	Percent Relative Standard Deviation	Average Percent Recovery
Amobam	4.6	50	45	3.5	7.8	90
	4.6	500	470	41	8.7	93
Busan 40	6.6	50	54	3.9	7.2	110
	6.6	500	510	31	6.1	100
Busan 85	5.9	50	56	3.0	5.5	110
	5.9	500	510	10	2.0	100
EXD	4.5	50	36	2.7	7.5	71
	4.5	500	380	9.1	2.4	76
Ferbam	5.2	50	47	2.2	4.8	94
	5.2	500	540	9.9	1.8	110
KN-Methyl	5.4	50	45	2.7	6.1	90
	5.4	500	440	11	2.5	89
Metham	6.2	50	53	2.8	5.2	110
	6.2	500	420	25	5.9	84
Nabam	4.8	50	31	2.0	6.6	62
	4.8	500	320	42	13	65
Nabonate	6.1	50	33	3.8	11	66
	6.1	500	280	33	12	56
NaDMDTC	5.4	50	53	1.3	2.5	110
	5.4	500	540	23	4.2	110
Thiram	4.5	50	44	1.3	2.9	89
	4.5	500	410	14	3.4	82
Zineb	5.2	50	44	1.5	3.4	87
	5.2	500	430	41	9.4	86
Ziram	5.7	50	50	5.9	12	100
	5.7	500	480	89	19	95

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The complete report, entitled "Determination of Dithiocarbamate Pesticides in Wastewaters," (Order No. PB 86-118 726/AS; Cost: $11.95, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

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